# Investigations of Crystalline Polarity Control of ZnO Thin Films

**2016 CNF iREU Intern: Caroline Zellhofer, Mechanical Engineering, University of Maryland, Baltimore County**

*CNF iREU Site: National Institute of Material Science (NIMS), Tsukuba, Ibaraki, Japan*
*CNF iREU Principal Investigator: Dr. Naoki Ohashi, National Institute for Materials Science*
*CNF iREU Mentor: Dr. Takeo Ohsawa, National Institute for Materials Science*
*Contact: crzellhofer@gmail.com, ohashi.naoki@nims.go.jp, ohsawa.takeo@nims.go.jp*

## Abstract:

**Zinc oxide (ZnO) thin films are a critical material used in many electronic applications, however a better understanding of the fundamental structure and origin of its properties is needed to continue improvements. This investigation studied the role of crystalline polarity in controlling the properties of ZnO thin films using *in situ* characterization techniques. Using a novel technique of applying a DC bias during sputtering to control the polarity, a change on polarity was found to correspond to a change in properties.**

## Summary of Research:

Zinc oxide (ZnO) thin films are a crucial material for electronic applications. ZnO is known for its transparent properties, n-type conductivity, piezoelectric properties, making it useful in applications, such as LEDS, solar cells, and varistors. In recent years, improvements to ZnO thin film properties have begun to plateau. A better understanding of the fundamental structure and origin of its properties is needed to continue improvements. The crystalline polarity of the ZnO thin films may hold the key to understanding the basis of its electrical and chemical properties, and how they can be controlled [1].

When ZnO is sputtered onto a substrate, on an atomic level the ZnO forms alternating layers of zinc and oxygen atoms. The thin film can terminate in either a zinc layer or oxygen layer, which is known as the crystalline polarity of the ZnO thin film [1]. Previously, the only approach to control the polarity of the film was to dope the film, usually with gallium or aluminum. This approach is expensive and time-intensive [2], but it also introduces free electrons into the material. Since there is no approach that isolates polarity from the addition of free electrons, which of the two fundamentally controls the properties is not known. In the Ohashi lab at NIMS, a novel approach was developed to control the polarity of the film independent of other factors. During sputtering, an external positive or negative DC bias was applied to the substrate, providing a simple, cost-effective, and time-efficient control on the polarity of the ZnO film [3].

For this study, Zn-terminated and O-terminated ZnO thin films were examined *in situ* on three commonly used substrates: glass, sapphire <0001>, and sapphire <11-20>. This study wished to investigate several questions. First, can consistent control over the polarity be established using the DC Bias method? Second, does the polarity control the electrical properties of the film? To test these questions, first ZnO was sputtered onto the chosen substrate using radio-frequency magnetron sputtering while a DC bias was applied to the substrate. Following sputtering, the thin film was analyzed *in situ* using x-ray photoelectron spectroscopy (XPS). In addition, the film was characterized using x-ray diffraction (XRD), Hall effect testing, gas sensing, and photo luminescence.

## Results and Conclusions:

First, comparing positive and negative applied biases on the three substrates, XRD analyses showed that for each substrate the crystals were forming normal to the <0001> direction regardless of the value of the bias. Thus, all crystals could be compared in other characterization tests. Using XPS, applying a positive bias corresponds to the spectra of a Zn-terminated film on glass, while applying a negative bias corresponds to an O-terminated film on glass. Both positive and negative biases applied to either sapphire substrate corresponded to O-terminated films, which can be seen in Figure 1.

Next, the substrates were characterized using Hall effect testing for their electrical properties, seen in Figure 2. Due to limitations of testing the sapphire substrates, they were not analyzed for electron density or electron mobility. Notably, between the

Zn-terminated and O-terminated films deposited on glass substrates, there are orders of magnitude differences between the resistance, electron density, and electron mobility. This proves that a change in polarity does create a change in thin film properties, and thus crystalline polarity is a controlling factor in the fundamental electrical properties of ZnO film.

Lastly, the substrates were analyzed using gas sensing. Gas sensing, seen in Figure 3, detects changes in resistance at various temperatures under exposure to gas, in this case, air and ethanol. For this test, only ZnO on glass was tested, due to limitations of testing the sapphire substrates. In Figure 4, the sensitivity is plotted, where the sensitivity, S, is the ratio of resistance of air, $R_a$, to the resistance of the gas mixture, $R_g$. As temperature increases for the ZnO/glass thin films, the Zn-terminated film grows more sensitive and then remains stable while the O-terminated film increases temporarily and then falls in sensitivity. This shows that in addition to changing the electrical properties, a change in polarity also corresponds to a change in gas sensitivity due to differences in thermal and chemical stability of the films.

In conclusion, the crystalline polarity of the film was shown to control the electrical and gas sensing properties of ZnO thin films. The DC Bias method was effective in controlling the polarity, and thus the ZnO properties, without doping the film. Further tests are needed to understand mechanisms behind ZnO properties in terms of polarity. Future work would include examining the mechanisms of the DC Bias method to understand the relationship between the substrate, the polarity, and the applied bias.

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## References:

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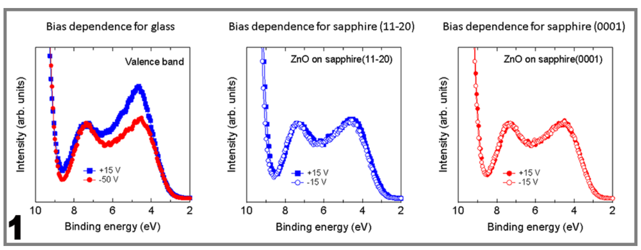


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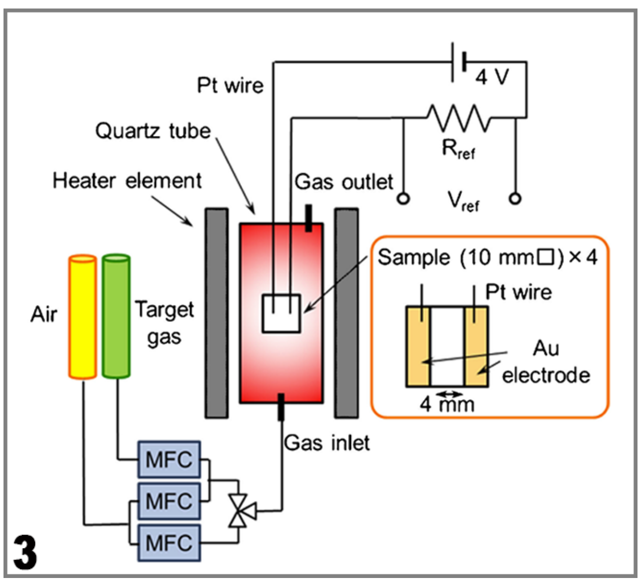
| Substrate | DC Bias (V) | Polarity | Resistivity (Ωcm) | Electron density ($cm^{-3}$) | Electron mobility ($cm^2V^{-1}s^{-1}$) |
|---|---|---|---|---|---|
| Silica glass | +15 | **Zn** | **0.5** | **$4.6 \times 10^{18}$** | **2.7** |
| Silica glass | -50 | **O** | **14.4** | **$1.4 \times 10^{19}$** | **$3.2 \times 10^{-2}$** |
| Sapphire (11-20) | +15 | O | 50.7 | - | - |
| Sapphire (11-20) | -15 | O | 54.7 | - | - |
| Sapphire (0001) | +15 | O | 58.5 | - | - |
| Sapphire (0001) | -15 | O | 38.7 | - | - |



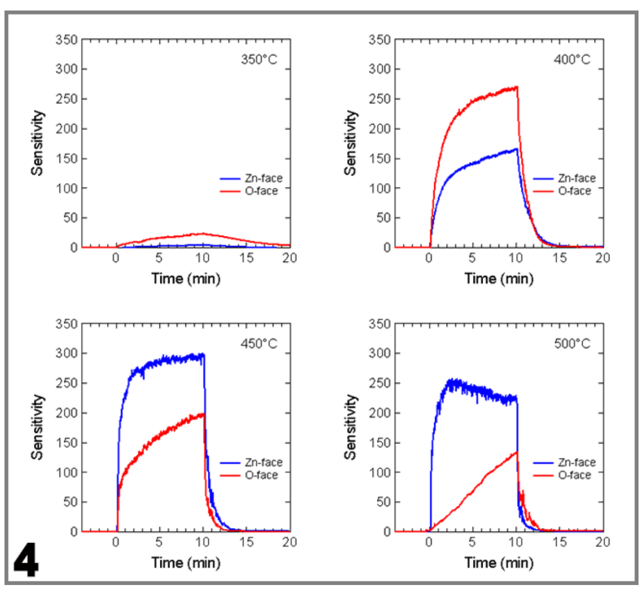




*Figure 1: XPS results for positive and negative applied biases on glass, sapphire <11-20>, and sapphire <0001>. Figure 2: Electrical properties of ZnO thin films. Figure 3: System used in gas sensing. Figure 4: Sensitivity of ZnO/glass under exposure to air and ethanol at different temperatures.*